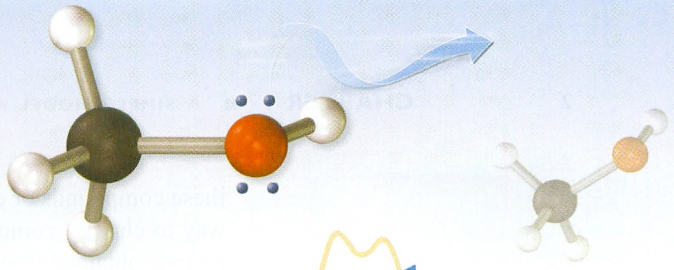
VISIT…



A Simple Model for Chemical Bonds

CHAPTER 1

MASTERING ORGANIC CHEMISTRY

- Drawing Lewis Structures
- Determining Formal Charges
- Estimating Stabilities of Structures
- Understanding Simple Examples of Resonance
- Recognizing Polar Bonds
- Determining Shapes of Molecules
- Determining Dipole Moments of Molecules

THIS CHAPTER begins your journey through the subject of organic chemistry. It starts with a brief overview of the field of organic chemistry to show why it is treated as a separate branch of chemistry. Most of the chapter is devoted to the development of a simple picture for the structure of molecules and the bonds that hold their atoms together. Lewis theory is used to explain ionic and covalent bonding. Other topics cover the formal charges of atoms in molecules, a brief introduction to resonance, polar bonds, the shapes of molecules, and polar molecules. Much of this material is a review of topics from general chemistry, but with an emphasis on applications to organic chemistry.

1.1 THE FIELD OF ORGANIC CHEMISTRY

The first question we might ask is "What is organic chemistry, and how did it become a separate branch of chemistry?" A brief survey of the history of organic chemistry will help us understand how the division of chemicals into organic and inorganic originated and why this division persists today.

Some chemical compounds that we today classify as organic, such as sugar, alcohol, and acetic acid (vinegar), have been known since antiquity. However, it was not until the late 1700s that Carl Wilhelm Scheele began his pioneering studies on the isolation of organic compounds. He isolated glycerol from animal fats, tartaric acid from grapes, lactic acid from sour milk, citric acid from lemons, and many other compounds. Neither Scheele nor the other chemists of that time knew the structures of

ORGANIC Chemistry Now™

Look for this logo in the text and go to OrganicChemistryNow at http://now.brookscole.com/hornback2 to view tutorials and simulations, develop problem-solving skills, and test your conceptual understanding with unique interactive resources.

these compounds or even which elements composed them. Because there was no better way to classify compounds, they were distinguished according to their sources. Compounds obtained from plants and animals were termed *organic* to indicate that their ultimate source was a living organism; those obtained from the mineral kingdom were termed *inorganic.*

This division according to source seemed reasonable, because both the physical and chemical properties of organic compounds are generally different from those of inorganic compounds. Typical organic compounds melt and boil at lower temperatures than typical inorganic compounds (salts). Organic compounds are more easily decomposed by heat than inorganic compounds are. These and other differences led many chemists of that time to believe that organic compounds still contained some of the life force of the organism that made them (the *vital force theory*).

Further progress in organic chemistry was provided by Antoine Lavoisier, who is often called the father of modern chemistry. In 1774 he demonstrated that organic compounds burn to produce carbon dioxide and water, meaning that they are composed predominantly of carbon, hydrogen, and perhaps oxygen. Later he showed that some organic compounds derived from animals also contain nitrogen.

In 1808 John Dalton proposed his atomic theory, making a major contribution to the understanding of inorganic compounds. Essentially, Dalton's theory postulated that the elements are composed of small, indivisible particles called atoms and that these atoms combine in ratios of small whole numbers to form chemical compounds.

Although the atomic theory helped explain the composition of many inorganic compounds, it did not help much in understanding the complexities of organic chemistry. In contrast to the relatively simple inorganic compounds that were known, such as H_2O, NO, and NO_2, there were a vast number of organic compounds, all composed of just a few elements but in a variety of ratios, such as C_2H_2, C_2H_4, C_2H_6, C_3H_8, and many, many more. Difficulties such as this led Jöns Berzelius, who coined the term *organic chemistry* in 1808 and who wrote the first text devoted to the subject in 1827, to wonder whether the atomic theory and other chemical laws even applied to organic compounds.

One tenet of the vital force theory, supported by Berzelius and other chemists of that time, was that only a living organism could make an organic compound. Friedrich Wöhler provided the first indication that this was not the case. In 1828 Wöhler found that urea, an organic compound, was formed when ammonium cyanate, an inorganic compound, was heated. Although this experiment contradicted the vital force theory, more commotion was caused at the time by the fact that both of these compounds have the same formula (CH_4N_2O) and were among the early examples of **isomers** (different compounds that have identical formulas).

Although we know today that there is no vital force that makes organic compounds different from those of the mineral world and that an organization based on source is often not appropriate, we still find it useful to divide compounds into the classes of organic and inorganic. However, today **organic chemistry** is defined as the study of the compounds of carbon. The division is still useful because of the unique chemical behavior of carbon and its compounds. Carbon forms strong single bonds to itself, and this allows chains of carbons to form. This results in an enormous variety of compounds. Organic compounds also behave quite differently from inorganic compounds. Special laboratory techniques have been developed to carry out and study organic reactions, to separate the complex mixtures of very similar compounds that are often produced, and to identify these products.

Although this division into organic and inorganic is useful in organizing the vast subject of chemistry, the division is somewhat arbitrary. For example, a compound that

contains both carbon and a metal, such as chlorophyll or hemoglobin, may be considered either organic or inorganic, depending on the interests of the person who is studying it. It is equally difficult (and unnecessary) to draw a line separating organic chemistry and biochemistry.

1.2 Simple Atomic Structure

To understand the structures of organic molecules and how these molecules react, we need a mental picture of the bonds that hold the atoms together. Several different models or pictures are used to describe the chemical bond. Which picture we use depends on what we are trying to accomplish. In this chapter we will learn about the simplest picture, which describes a covalent bond as a shared pair of electrons and uses Lewis structures to represent molecules. Although this model is not complex, it will be adequate for most of our uses. (In Chapter 3 we will look at a more complex model for bonding.) Most of what is covered in this chapter should be a review.

Before looking at molecules, we need to review the structure of atoms. Most of the mass of an atom is concentrated in the **nucleus.** The nucleus consists of **protons,** which are positively charged, and **neutrons,** which are neutral. To counterbalance the charge on the nucleus due to the positive protons, the atom has an equal number of negative **electrons** in **shells** or **orbitals** around the nucleus. Because the electrons in the outermost electron shell (the **valence electrons**) control how the atom bonds, atoms are often represented by their respective atomic symbol surrounded by dots representing the outer-shell electrons. Such representations for some of the elements of interest to us are shown in Figure 1.1. The number of electrons in the **valence shell** of an atom is the same as the group number of that atom in the periodic table.

PROBLEM 1.1

Show Lewis structures for these atoms:

a) Bromine **b)** Calcium **c)** Germanium

In the simplest model, bonding can be considered to result from the special stability associated with a filled outer shell of electrons. The noble gases, such as helium, neon, and argon, which already have a filled outer shell of electrons, have little tendency to form bonds. Atoms of the other elements, however, seek to somehow attain a filled outer shell of electrons. The two ways in which they accomplish this goal result in two types of bonding: ionic and covalent.

Group number	1A	2A	3A	4A	5A	6A	7A	8A
	H·							He:
	Li·	·Be·	·B·	·C·	·N·	·O·	:F·	:Ne:
	Na·	·Mg·	·Al·	·Si·	·P·	·S·	:Cl·	:Ar:

Figure 1.1

LEWIS STRUCTURES FOR SOME ATOMS OF INTEREST IN ORGANIC CHEMISTRY. The atomic symbol represents the nucleus and the inner-shell electrons. The dots represent the electrons in the outer shell (valence shell).

1.3 Ionic Bonding

In **ionic bonding,** we picture the atoms as gaining or losing electrons to arrive at the same number of electrons as one of the noble gases. Because electrons are charged, this gain or loss results in the formation of charged atoms or ions. This type of bonding is common when metals from the left side of the periodic table combine with nonmetals from the right side. Two examples, the formation of lithium fluoride and magnesium oxide, are shown in Figure 1.2.

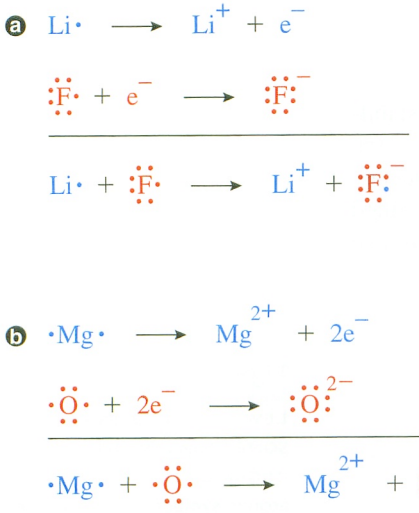
PROBLEM 1.2

Show reaction equations using Lewis structures for the formation of these compounds from their elements:

a) Calcium chloride **b)** Sodium sulfide

Because ions with opposite charges attract each other, an ionic bond results from the attractive force between the positively charged cation and the negatively charged anion. A typical ionic compound is a high-melting solid. In the solid crystal, several anions surround each cation. Each of these anions is attracted equally to the cation. Likewise, each anion is surrounded by several identical cations that are equally attracted to the anion. Because of these multiple interactions, we cannot say that a particular cation is bonded to a particular anion. Therefore, we do not speak of a molecule of an ionic compound, because this would imply one cation associated with one anion.

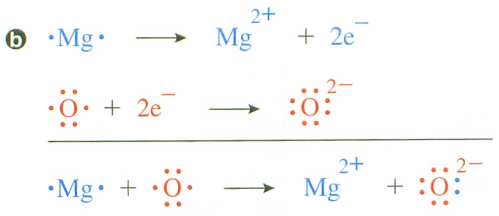
The attractive interactions of each cation with a number of anions and vice versa result in a network of strong attractive forces that extend throughout the whole crystal. We can think of these as a three-dimensional net of attractive forces. Disrupting these forces requires a large amount of heat energy; therefore, ionic compounds usually have



The easiest way for lithium to attain a noble gas configuration is for it to lose one electron. The resulting lithium cation has the same number of electrons as helium.

Fluorine prefers to gain one electron. The fluoride anion has the same number of electrons as neon.

These two reaction equations can be summed (the electrons cancel) to show the formation of lithium fluoride, an ionic compound.



Magnesium can lose the two electrons in its valence shell and attain the electronic configuration of neon.

Oxygen can attain the electronic configuration of neon by gaining two electrons.

These two reaction equations can be summed to show the formation of magnesium oxide, an ionic compound.

Figure 1.2

THE FORMATION OF ⓐ LITHIUM FLUORIDE AND ⓑ MAGNESIUM OXIDE.

high melting points and high boiling points. For example, the melting point of magnesium chloride is 708°C, and its boiling point is 1412°C.

For carbon to attain the electronic configuration of a noble gas by this method, it would have to lose or gain four electrons. This would result in a C^{4+} cation (helium configuration) or a C^{4-} anion (neon configuration). The high concentration of charge in a small volume in both of these ions makes them unstable, high-energy species. Because of this high charge-to-volume ratio, carbon prefers to attain the electronic configuration of the noble gases in another manner—that is, by covalent bonding. Many other atoms also attain stable electronic configurations in this manner.

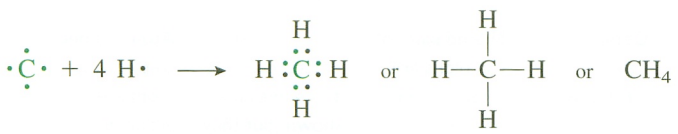
1.4 Covalent Bonding

In **covalent bonding,** we picture atoms as sharing electrons to arrive at the same number of electrons as a noble gas. The shared electrons are counted as part of the total electrons for both of the atoms involved in the bond. Consider the simple example of the formation of the hydrogen molecule from two hydrogen atoms. Each hydrogen atom has one electron in its valence shell, and each would like to have two (helium configuration). If the two hydrogen atoms come together, each bringing one electron, they can share these electrons. Each hydrogen of the resulting molecule experiences two electrons in its valence shell. The shared pair of electrons in a covalent bond is often represented by a line, as in the middle structure that follows:

$$H\cdot + H\cdot \longrightarrow H:H \quad \text{or} \quad H{-}H \quad \text{or} \quad H_2$$

In this case, one hydrogen is strongly bonded to the other hydrogen. We can, therefore, speak of these two hydrogen atoms as forming a hydrogen molecule. However, the attractive force between this hydrogen molecule and other hydrogen molecules is quite weak. Because only a small amount of heat energy needs to be added to overcome this weak force and separate individual hydrogen molecules, hydrogen has very low melting and boiling points, near absolute zero (mp = −259°C, bp = −252°C) and is a gas at normal temperatures and pressures. In general, covalent compounds have strong bonds between the atoms of the molecule itself but only weak attractions for other molecules. Therefore, covalent compounds melt and boil at much lower temperatures than do ionic compounds.

Carbon is central to the study of organic chemistry, so let's consider its bonding. Carbon has four electrons in its valence shell. It can attain the electronic configuration of neon (eight electrons in its valence shell) by using each of these electrons, along with four electrons from other atoms, to form four covalent bonds. Thus, the simplest compound of carbon and hydrogen results from the combination of four hydrogen atoms with one carbon atom to produce methane, CH_4. Again, each covalent bond is strong, but the attraction between individual methane molecules is weak. Methane melts at −182°C and boils at −164°C.



Methane

1.5 Lewis Structures

Structures in which all the electrons in the valence shells are shown as dots are called **Lewis structures.** The Lewis structure for H_2O is shown in Figure 1.3. Drawing larger molecules in this fashion can be rather tedious, but there are a number of shorthand ways to represent molecules. For instance, see the previous example for CH_4 and Figure 1.3 for water. All of these representations for water describe the same molecule. Whenever we look at a structure, we should examine it carefully to be sure that we understand exactly what is meant. For example, if we see water represented by the third structure in Figure 1.3, we must realize that oxygen has two unshared pairs of electrons that have not been shown. If these unshared pairs of electrons were not present, the structure would represent a highly unstable and unusual ionic species. *Any unusual feature of a structure must be shown explicitly.* Until you become more familiar with these various ways to represent structures, you should carefully examine each structure that you encounter and picture the complete Lewis structure, including any unshared electron pairs that have not been explicitly shown.

We need to learn the number of bonds that are commonly formed by the atoms that are important in organic chemistry. In the vast majority of cases, hydrogen forms one covalent bond so that it has two electrons in its outer shell. In covalent compounds the atoms of the second period (or row) of the periodic table need eight electrons in their outer shell. (This is called the **octet rule.**) We have already seen that to accomplish this carbon forms four bonds. In a similar fashion we can determine the number of bonds that some other second-period atoms prefer to form. The number of bonds that commonly occur in neutral molecules for the elements of most interest in organic chemistry are listed in Table 1.1.

PROBLEM 1.3

Show Lewis structures for the simplest neutral compounds formed from these elements:

a) Carbon and chlorine **b)** Hydrogen and bromine

Although the number of bonds shown in Table 1.1 yields neutral structures and is the most common number for each of these elements, other bonding arrangements are also encountered. For example, in some cases, oxygen forms a third bond by using a

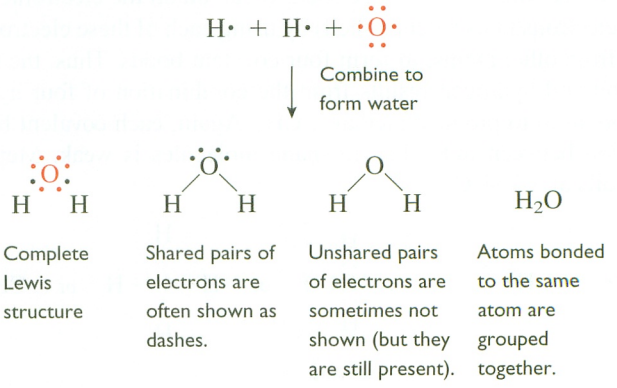
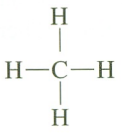
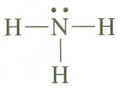
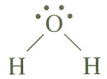

H· + H· + ·O·
Combine to form water
Complete Lewis structure
Shared pairs of electrons are often shown as dashes.
Unshared pairs of electrons are sometimes not shown (but they are still present).
Atoms bonded to the same atom are grouped together.
H2O

Figure 1.3

VARIOUS METHODS USED TO REPRESENT THE STRUCTURE OF WATER.

Table 1.1 Number of Bonds Commonly Formed by Some Elements

Atom	Common Number of Bonds	Example		
H	1	H—H	or	H_2
C	4		or	CH_4
N	3		or	NH_3
O	2		or	H_2O
X*	1		or	HBr

*X is used to represent all of the halogens, F, Cl, Br, and I.

pair of its unshared electrons. In such situations the oxygen provides both electrons for the bond that it forms with an electron-poor atom. However, the oxygen still has eight electrons in its outer shell. More examples like this are presented in Chapter 2.

We can also use Table 1.1 to tell us the number of bonds preferred by other atoms that are from the same columns (or groups) of the periodic table as those shown in the table. Elements from the same group have the same number of electrons in their valence shells. Therefore, they form the same number of bonds, and in general, they have similar chemistries. Thus, silicon, being in the same column as carbon, prefers to form four bonds. Phosphorus, like nitrogen, prefers three bonds, whereas sulfur, being related to oxygen, prefers two. All of the halogens (F, Cl, Br, I) form covalent compounds with one bond. However, elements from the third and subsequent periods of the periodic table may have more than 8 electrons in their outer shells (10 and 12 electrons are both common) and may therefore form more than the number of bonds suggested by Table 1.1. These cases will be discussed in more detail later.

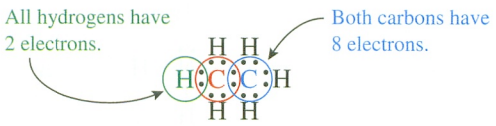
PROBLEM 1.4

Show a Lewis structure for the simplest neutral compound formed from hydrogen and sulfur.

It is useful to be able to look at a Lewis structure and judge the stability of the compound represented by that structure. Can the compound be isolated and put in a bottle? Is it more stable than another, similar compound? The most important factor to examine in determining whether a molecule is stable is whether the octet rule is satisfied. Compounds with fewer than eight electrons around a second-period atom are known but are seldom stable. (However, such compounds are encountered as unstable, highly reactive intermediates in some chemical reactions.) Furthermore, compounds with more

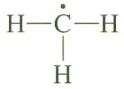
than eight electrons around a second-period atom are also unstable. In stable molecules, hydrogen strongly prefers to have two electrons. (Later, we will examine some of the more subtle factors that affect stability.)

Let's consider ethane as an example. The formula for ethane, C_2H_6, does not provide enough information for us to judge its stability. We need to examine its structure. The Lewis structure for ethane shows that the octet rule is satisfied for both carbons, and each hydrogen has two electrons. Therefore, ethane is predicted to be a stable compound—and it is.



PRACTICE PROBLEM 1.1

Discuss the stability of the following species:

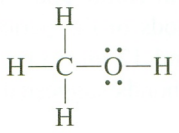


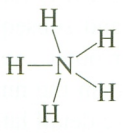
Solution

This species has a total of seven electrons around the carbon. Because the octet rule is not satisfied, the molecule is predicted to be unstable. (However, we will encounter this and related species as unstable intermediates in some chemical reactions in later chapters.)

PROBLEM 1.5

Discuss the stability of these structures:

a) 

b) 

We need to be able to write a stable Lewis structure for a compound whose formula is provided. As an example, let us write a Lewis structure for CH_4O. First, how many electrons should be used? CH_4O is neutral, so the total electrons shown in the structure must be the same as the total in the valence shells of the neutral atoms involved. In this case the carbon contributes 4 electrons, each hydrogen contributes 1, and the oxygen contributes 6, for a total of 14. This is one way of counting electrons to ensure that the compound is neutral. If the compound were charged, there would be one electron less than this total for each unit of positive charge or one electron more than this total for each unit of negative charge. We then try to assemble the atoms into a structure that satisfies the octet rule. This can often be done by bonding the atoms other than hydrogen together and then filling the valences with the hydrogens. This process is shown in Figure 1.4 for CH_4O.

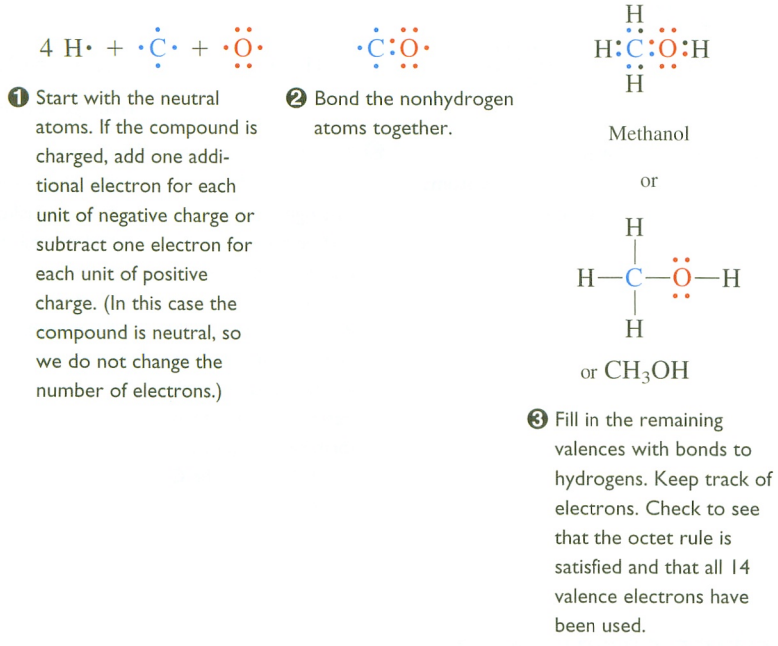

4 H· + ·C· + ·O·
❶ Start with the neutral atoms. If the compound is charged, add one additional electron for each unit of negative charge or subtract one electron for each unit of positive charge. (In this case the compound is neutral, so we do not change the number of electrons.)
·C:O·
❷ Bond the nonhydrogen atoms together.
H:C:O:H
Methanol
or
H—C—O—H
or CH3OH
❸ Fill in the remaining valences with bonds to hydrogens. Keep track of electrons. Check to see that the octet rule is satisfied and that all 14 valence electrons have been used.

Figure 1.4

WRITING A LEWIS STRUCTURE FOR METHANOL, CH_4O.

Sometimes more than one bond is needed between elements that have a valence greater than 1. If using only single bonds between atoms results in too few electrons to satisfy the octet rule for all of the atoms, then additional electron sharing between atoms must occur, resulting in the formation of double or triple bonds. For each two electrons needed to complete the octets of the atoms in the molecule, one additional bond between two of the atoms must be formed. This process is illustrated in Figures 1.5 and 1.6 for C_2H_4 and HCN, respectively.

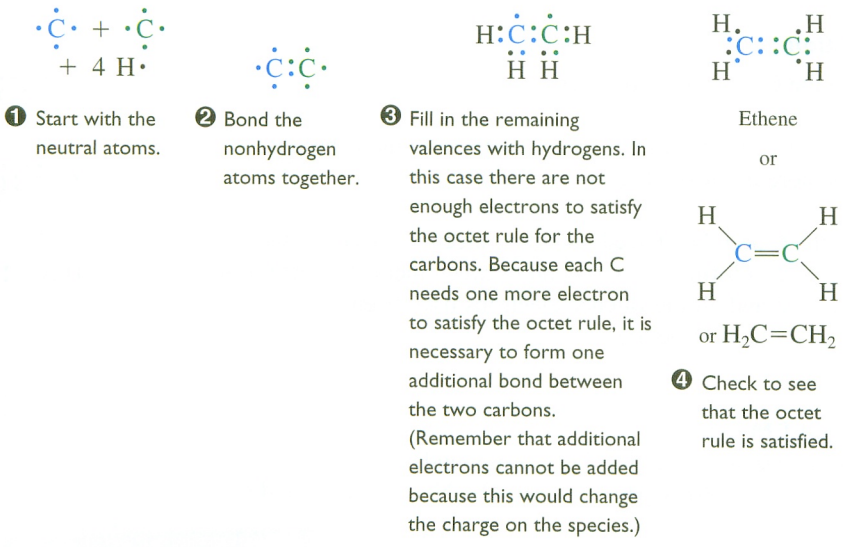
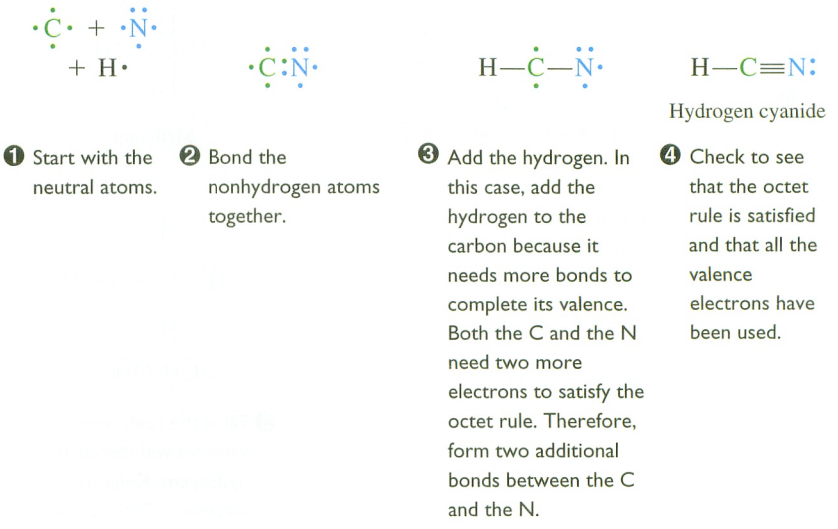

·C· + ·C·
+ 4 H·
❶ Start with the neutral atoms.
·C:C·
❷ Bond the nonhydrogen atoms together.
H:C:C:H
H H
❸ Fill in the remaining valences with hydrogens. In this case there are not enough electrons to satisfy the octet rule for the carbons. Because each C needs one more electron to satisfy the octet rule, it is necessary to form one additional bond between the two carbons. (Remember that additional electrons cannot be added because this would change the charge on the species.)
Ethene
or
C=C
or H2C=CH2
❹ Check to see that the octet rule is satisfied.

Figure 1.5

WRITING A LEWIS STRUCTURE FOR ETHENE, C_2H_4.

Figure 1.6

WRITING A LEWIS STRUCTURE FOR HYDROGEN CYANIDE, HCN.


Hydrogen cyanide
❶ Start with the neutral atoms.
❷ Bond the nonhydrogen atoms together.
❸ Add the hydrogen. In this case, add the hydrogen to the carbon because it needs more bonds to complete its valence. Both the C and the N need two more electrons to satisfy the octet rule. Therefore, form two additional bonds between the C and the N.
❹ Check to see that the octet rule is satisfied and that all the valence electrons have been used.

PRACTICE PROBLEM 1.2

Write a Lewis structure for CH_2O.

Strategy

Follow the same process used in Figures 1.5 and 1.6.

1. Start with the neutral atoms and bond the nonhydrogen atoms together.
2. Add the hydrogens.
3. If the valences of the atoms are not satisfied, form additional bonds between the atoms.
4. Check to see that the octet rule is satisfied at all atoms.

Solution

Bond the C and the O together.

Add the hydrogens. In this case, add them to the C because it has more unsatisfied valences.

Both the C and the O need one more electron to satisfy the octet rule, so form a second bond between them. The octet rule is satisfied and all the valence electrons have been used, so this is an acceptable structure.

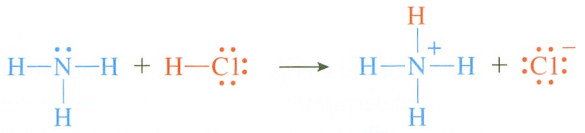
PROBLEM 1.6

Write Lewis structures for these compounds:

a) C_3H_8 **b)** C_2H_2 **c)** CH_3N **d)** NH_3O

1.6 COVALENT IONS

We will encounter many covalent compounds that have a charge. This results in ionic compounds that have covalent cations, covalent anions, or both. For example, consider the following acid–base reaction between ammonia and hydrogen chloride to produce ammonium chloride. How do we determine that NH_4 is a cation with a charge of +1 while Cl is an anion with a charge of −1? Several different methods can be used to determine the charge on a Lewis structure. Because charge is determined by the number of protons and electrons, we can simply subtract the total electrons from the protons. In the case of the ammonium cation, there are 7 protons from the nitrogen plus 4 from the 4 hydrogens minus 10 electrons (8 shown in the Lewis structure and the 2 electrons from the 1*s* shell of the nitrogen). This totals to a charge of +1 (7 + 4 − 10 = +1).



Another way to determine charges is to remember that charge must balance in a chemical reaction. In the previous reaction, the total charge on the left side of the equation is zero. Therefore, the total charge on the right side of the equation must also sum to zero. Because we have already calculated that the charge on the ammonium cation is +1, the charge on the chloride anion must be −1. Learn to visualize reactions in terms of the charges involved. In the preceding reaction, a hydrogen, without any electrons, is transferred from Cl to N. Because a hydrogen without electrons is a proton, the reaction has transferred one unit of positive charge from Cl to N.

PROBLEM 1.7

Using Lewis structures, show a balanced equation for the reaction of H_2O with HCl.

The final method of determining charge, and the one most useful to us, is the method of formal charges.

1.7 FORMAL CHARGES

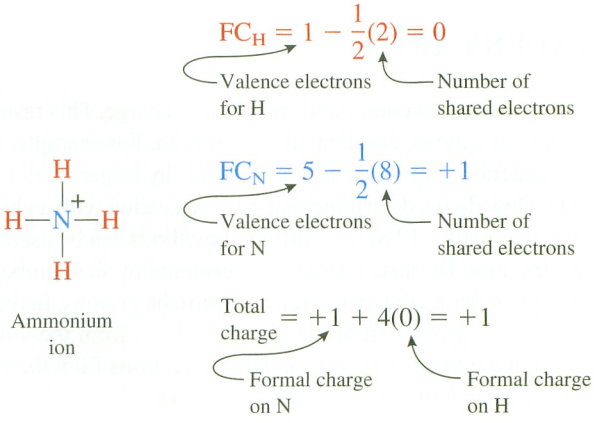
Formal charge is a method used to assign an approximate charge distribution among the atoms of a covalent species, regardless of whether it is ionic or neutral overall. The **formal charge** on an atom is defined as the number of valence electrons in the neutral atom before any bonding (this is the same as the group number of the atom) minus the number of unshared electrons on the atom in the structure of interest and also minus one-half the number of shared electrons on that atom:

$$\text{formal charge} = \begin{pmatrix}\text{valence electrons}\\ \text{in the atom}\end{pmatrix} - \begin{pmatrix}\text{number of}\\ \text{unshared electrons}\end{pmatrix} - \frac{1}{2}\begin{pmatrix}\text{number of}\\ \text{shared electrons}\end{pmatrix}$$

Calculation of the formal charges on the atoms of the ammonium ion is shown in Figure 1.7. Note that the sum of the formal charges on all the atoms of a covalent molecule gives the total charge on that molecule.

Figure 1.7

CALCULATING THE FORMAL CHARGES FOR AMMONIUM ION, NH_4^+.

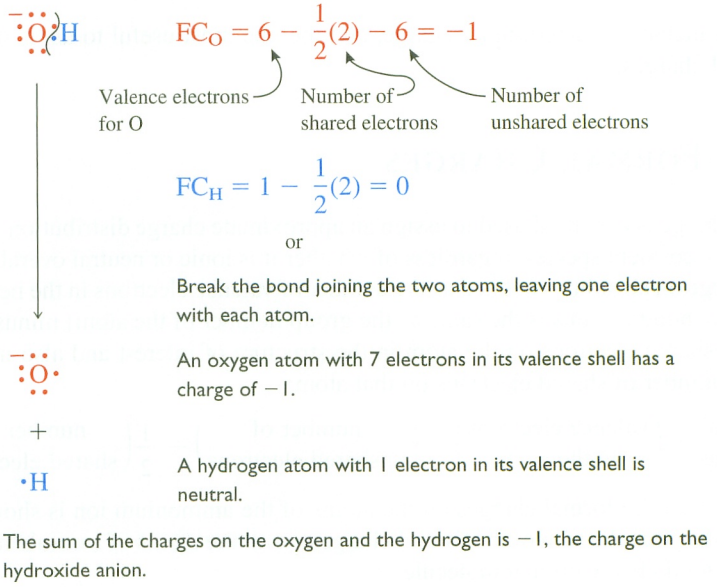

$FC_H = 1 - \frac{1}{2}(2) = 0$
Valence electrons for H
Number of shared electrons
$FC_N = 5 - \frac{1}{2}(8) = +1$
Valence electrons for N
Number of shared electrons
Ammonium ion
Total charge $= +1 + 4(0) = +1$
Formal charge on N
Formal charge on H

It will help us to understand formal charges if we analyze the process of calculating these charges. Basically, we are determining charge by counting protons and electrons as we did in the first method described earlier. If all the valence electrons were somehow stripped from the atom, the remaining ion would have a total positive charge equal to the group number. We subtract from this positive charge the "average" number of electrons (negative charges) that are around the atom in the Lewis structure. The average number of electrons around the atom is the sum of the unshared electrons (these spend all of their time around the atom) plus one-half of the shared electrons (these spend only one-half of their time around each of the atoms sharing them).

Another way to view this process is to imagine symmetrically breaking all the bonds to an atom—that is, keeping one electron from each bond with each atom. The formal charge can then be calculated by determining the charge on the resulting species. This process is shown for hydroxide ion in Figure 1.8.

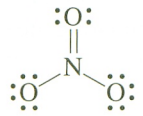
Figure 1.8

CALCULATING THE FORMAL CHARGES FOR HYDROXIDE ION, OH^-.


$FC_O = 6 - \frac{1}{2}(2) - 6 = -1$
Valence electrons for O
Number of shared electrons
Number of unshared electrons
$FC_H = 1 - \frac{1}{2}(2) = 0$
or
Break the bond joining the two atoms, leaving one electron with each atom.
An oxygen atom with 7 electrons in its valence shell has a charge of −1.
A hydrogen atom with 1 electron in its valence shell is neutral.
The sum of the charges on the oxygen and the hydrogen is −1, the charge on the hydroxide anion.

PRACTICE PROBLEM 1.3

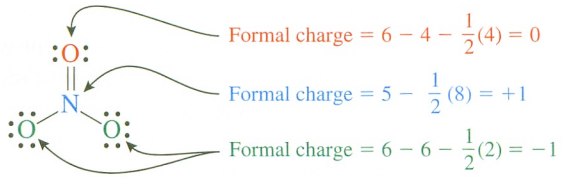
Calculate the formal charges on each atom of this species:



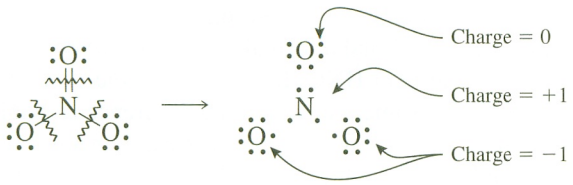
ORGANIC Chemistry Now™
Click *Coached Tutorial Problems* to practice **Calculating Formal Charges.**

Solution

The formal charges can be calculated from the equation:



The formal charge can also be calculated from the species produced by breaking each bond so that one electron of the bond remains with each atom:

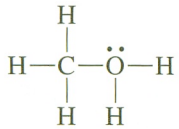


The total charge is $0 + 1 + (-1) + (-1) = -1$.

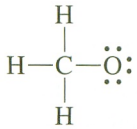
PROBLEM 1.8

Calculate the formal charges on each of the atoms, except hydrogens, of these molecules and determine the total charge of the species:

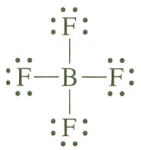
a)



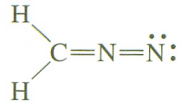
b)



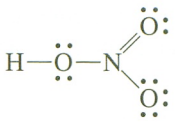
c)



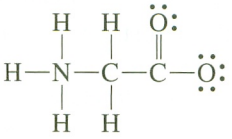
d)



e)



f)



Glycine (an amino acid)

BioLink

As you continue to study organic chemistry, you will begin to recognize the formal charges on many atoms without doing any calculations. Most atoms in covalent compounds have formal charges of zero. For example, a carbon with four bonds is neutral, as is an oxygen with two bonds and two unshared pairs of electrons. An oxygen with only one bond and three unshared pairs of electrons has a formal charge of −1.

The most important criterion for estimating the stability of a compound represented by a particular Lewis structure is whether or not the structure satisfies the octet rule. Formal charges can be used to refine estimates of stability. Because unlike charges attract, energy is required to separate positive and negative charges. (Similarly, like charges repel, so energy is required to bring them together.) Therefore, the presence of formal charges will destabilize a molecule. This does not mean that any structure with formal charges represents an unstable molecule. It does mean that structures with fewer formal charges will be more stable, other things being equal.

As an example, consider the molecule formed from one atom each of carbon, hydrogen, and nitrogen. We can assemble these atoms in two different ways and still satisfy the octet rule. (This is another example of compounds that have the same molecular formula but a different arrangement of bonded atoms. Such compounds are called **constitutional isomers** or **structural isomers** and are very common in organic chemistry.) The structure on the left was the one used in Figure 1.6. The structure on the right is obtained if the hydrogen is bonded to the N rather than the C.

Because HCN has formal charges of zero on all the atoms, whereas HNC has a formal charge on nitrogen of +1 and a formal charge on carbon of −1, we would expect HCN to be more stable than HNC. Indeed, this is the case. We will encounter many cases of constitutional isomers in which the difference in stability is much less than in this example. In such cases, much more subtle arguments must be used to predict which is more stable, if a prediction can be made at all without experimental measurements.

PROBLEM 1.9

Predict which of the following constitutional isomers for the compound that is formed from one atom each of hydrogen, oxygen, and chlorine is more stable:

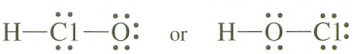
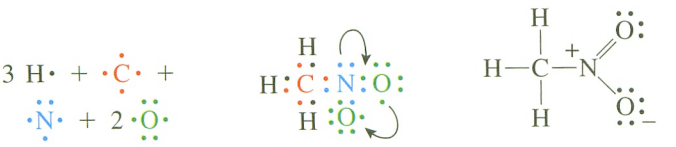


Figure 1.9 illustrates the construction of a Lewis structure for a more complex example, nitromethane. In this case there are a number of reasonable (according to what we know now) constitutional isomers. Therefore, we must be told the **connectivity,** or which atoms are bonded to which. Once the connectivity shown in Figure 1.9 is given, the best structure that satisfies the octet rule has some formal charges. This still represents a quite stable molecule.

The structure shown for nitromethane in Figure 1.9 is not quite consistent with experimental data. According to this structure, the two oxygens are different. One has a single bond to the nitrogen and a formal charge of −1; the other has a double bond to nitrogen and a formal charge of zero. However, various experiments have shown that these two oxygens are, in fact, identical. Their bonds to nitrogen have identical lengths and strengths, between those of single and double bonds, and they have the same



❶ Start with the uncombined atoms. There are a number of plausible structural isomers, so we must be told the connectivity. Nitromethane has the H's bonded to the C, the C bonded to the N, and both O's bonded to the N.

❷ This first attempt results in a structure that needs two more electrons to satisfy the octet rule at all of the atoms. Therefore, a double bond must be present. The arrows show how we mentally picture moving the electrons to accomplish this.

❸ This structure satisfies the octet rule. Although it has a formal charge on N of +1 and a formal charge on one of the O's of −1, it is the best that can be done with the given connectivity. Nitromethane is a stable molecule that can be isolated.

Figure 1.9
WRITING A LEWIS STRUCTURE FOR NITROMETHANE, CH_3NO_2.

charge. To explain situations like this, in which the Lewis structure does not give an accurate picture of the molecule, the concept of resonance is employed.

1.8 RESONANCE

As shown in Figure 1.10, two Lewis structures can be written for nitromethane. These structures are different because one has a double bond to one oxygen, whereas the other has a double bond to the other oxygen. Obviously, these structures are equally good representations for nitromethane, because they are of equal stability.

In cases such as this, neither structure is an accurate representation of the actual structure. The actual structure is a **resonance hybrid** of these two structures. It is a blend of the extremes represented by these two structures. For example, one of the structures has a double bond between the nitrogen and one of the oxygens, but these same two atoms are connected by a single bond in the other structure. The actual bond between the nitrogen and this oxygen is more than a single bond but less than a double bond. The same analysis applies to the other oxygen, so the bonds to both of these oxygens are identical. Furthermore, because each oxygen is neutral in one resonance structure and has a negative charge in the other structure, the actual charge on each in the resonance hybrid is one-half of a full negative charge.

The last structure in Figure 1.10 is an attempt to show a structure for the resonance hybrid. Because there are partial bonds (represented by the dashed lines) between the nitrogen and the oxygens and there is a pair of electrons that is shared by the two oxygens, even though they are not directly bonded, this structure looks strange. It is difficult to determine whether the octet rule has been satisfied for the oxygens and the nitrogen. Rather than trying to represent such molecules by structures that might be confusing, normal Lewis structures and resonance arrows are used.

Just as the first structure in Figure 1.10 is not an accurate representation of the actual structure of nitromethane, it also does not provide a basis for an accurate estimate of the stability of nitromethane. The compound is more stable than either of the resonance structures would indicate. This extra stability is called the **resonance stabilization energy.**

Figure 1.10

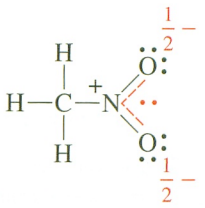
RESONANCE STRUCTURES FOR NITROMETHANE.

Nitromethane

Two equivalent structures can be written for nitromethane. These are different if it is specified that no atoms have moved.

The double-headed arrow is used to indicate that the actual structure is a resonance hybrid of these two structures.

Because both structures are equivalent, they make equal contributions to the hybrid.



The actual structure is a blend of the two resonance structures. This structure is an attempt to represent the hybrid structure using dashed lines to indicate partial bonds. It has a partial double bond to each oxygen and an unshared pair of electrons that is located partly on each oxygen. Rather than using confusing structures like this, we use regular Lewis structures and the resonance arrow.

We will use resonance often, so it is important to understand exactly what it means. Resonance does not mean that the structure of the molecule is changing back and forth between the structures in the case of nitromethane. It does not mean that the bond to one of those oxygens is a double bond part of the time and a single bond the rest of the time. Instead, the structure is static, an average of the individual structures. *The double-headed **resonance arrow** is used only for resonance and should not be confused with the **equilibrium arrows,** which are used to represent an equilibrium reaction in which the molecules are indeed changing structures.*

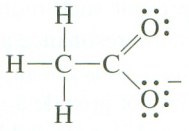
Important Convention

Resonance arrow ⟷ Equilibrium arrows ⇌

Resonance must be used whenever more than one reasonable Lewis structure can be written for a molecule, provided that the Lewis structures have *identical positions of all atoms.* Only the positions of unshared electrons and multiple bonds are changed in writing different resonance structures. When a better picture of bonding is developed in Chapter 3, we will get a better understanding of what resonance means and when it must be used.

PROBLEM 1.10

Experimental evidence indicates that the two oxygens of acetate ion are identical. Use resonance to explain this observation.



Acetate ion

1.9 Polar Bonds

In calculations of formal charge, we assume that a shared pair of electrons spends equal time around both of the atoms that form the bond. This is true only if the atoms are the same. More commonly, the bond is between two different atoms, and the electrons are not necessarily shared equally. The atom that has a greater share of the electrons can be determined from the **electronegativities** (electron-attracting abilities) of the atoms involved in the bonds. The electron density represented by a pair of shared electrons is greater around the atom with the greater electronegativity.

Table 1.2 lists the electronegativities of the atoms that are of most interest to organic chemists. Remember that electronegativities increase from left to right (excluding the noble gases) in a period of the periodic table and also from bottom to top in a column. For our purposes we can consider carbon and hydrogen to have roughly the same electronegativity. The order of electronegativities of the atoms of most interest to us is as follows:

$$\mathrm{H} \approx \mathrm{C} < \mathrm{Br} < \mathrm{Cl} = \mathrm{N} < \mathrm{O} < \mathrm{F}$$

increasing electronegativity

Because the electrons in a covalent bond spend more time around the more electronegative atom, this atom has more negative charge around it than the formal charge indicates. Consider the hydrogen chloride molecule. The formal charges on both atoms in the Lewis structure are zero. However, chlorine is more electronegative than hydrogen. Therefore, the shared electrons spend more time around the chlorine than around the hydrogen. The chlorine has more electron density around it than the Lewis structure indicates and thus has some negative charge associated with it. Similarly, the hydrogen has less electron density and some positive charge. Because the electrons of the covalent bond are still shared, although unequally, the amount of charge on each atom is less than 1. There is a partial negative charge on the chlorine and a partial positive charge on the hydrogen. The lowercase Greek letter delta (δ) followed by the sign of the charge is used to represent such partial charges:

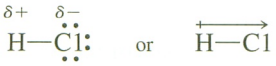


Table 1.2 Pauling Scale of Electronegativity Values for Some Elements

Group						
1A	2A	3A	4A	5A	6A	7A
H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2		Si 1.8	P 2.1	S 2.5	Cl 3.0
						Br 2.8
						I 2.5

When unequal electronegativities of two atoms involved in a bond result in charge separation as just described, we say that the bond is **polar.** Hydrogen chloride has a polar bond. The charge separation results in a **dipole,** that is, a positive and a negative "pole" in the molecule. The product of the amount of charge separation (e) times the distance of the charge separation (d) is called the **dipole moment** (μ).

$$\mu = (e)(d)$$

The dipole moment is a vector; that is, it has direction and magnitude. The dipole moment is usually represented as an arrow pointing from the positive end to the negative end of the dipole, as shown earlier for hydrogen chloride.

The amount of the charge, e, is on the order of 10^{-10} electrostatic units (esu), and the distance, d, is on the order of 10^{-10} m, so μ is on the order of 10^{-20} esu m. The debye unit (D) is defined as 1×10^{-20} esu m. The dipole moment of HCl is 1.1 D.

The direction and relative magnitude of the dipole of any bond can be predicted from the electronegativities of the atoms involved in the bond. For example, the electrons of a bond between oxygen and carbon will spend more time around the oxygen because it is more electronegative; therefore, the oxygen will be the negative end of the bond dipole. In the case of a bond between carbon and hydrogen, the two elements are of similar electronegativities. Therefore, the electrons are shared nearly equally, resulting in a slightly polar bond that is usually considered to be a **nonpolar bond.**

PROBLEM 1.11

Show the direction of the dipoles, if any, of these bonds:

a) C—N **b)** O—N **c)** O—Cl **d)** C—Cl
e) B—O **f)** C—Mg **g)** C—C **h)** C—H

The concept of bond polarities is very important, because much of chemistry, both the physical properties of compounds and their chemical reactions, depends on the interaction of charges. For example, a reagent that is seeking positive charge will likely be attracted to the carbon of a carbon–oxygen bond.

So far, we are able to predict the dipoles of individual bonds. The overall dipole moment of a molecule is the vector sum of these individual bond dipoles. Before the bond dipoles can be used to predict the overall dipole moment of a molecule, however, the three-dimensional orientation of the bonds must be known. That is, we need to know the shapes of molecules.

1.10 Shapes of Molecules

The shapes of molecules are determined by actual experiments, not by theoretical considerations. But we do not want to have to memorize the shape of each molecule. Instead, we would like to be able to look at a Lewis structure and predict the shape of the molecule. Several models enable us to do this. One of the easiest to use is **valence shell electron pair repulsion theory,** which is often referred to by its acronym *VSEPR* (pronounced "vesper"). As the name implies, the theory states that pairs of electrons in the valence shell repel each other and try to stay as far apart as possible. You probably remember this theory from your general chemistry class. The parts of VSEPR theory that

are most important to organic chemistry will be reviewed here. The rules that are needed are as follows:

▶ RULE 1

Pairs of electrons in the valence shell repel each other and therefore stay as far apart as possible. For example, if four pairs of electrons are arranged around a central atom so that they are as far apart as possible, they will be located at the corners of a tetrahedron. The geometries resulting from other numbers of electron pairs, arranged as far apart as possible, are given in Figure 1.11.

When we attempt to show the shapes of molecules, we are faced with the problem of how to represent such three-dimensional objects on paper. Some bonds extend in

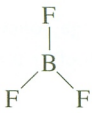
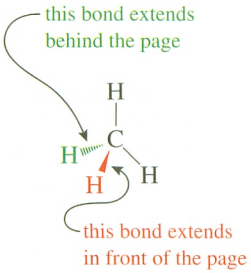
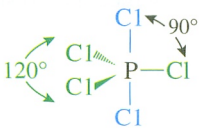
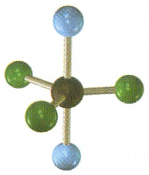
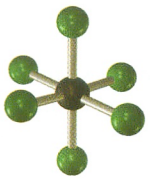
Number of Electron Pairs	Geometry	Example	
2	linear	Cl—Be—Cl	
3	trigonal planar		
4	tetrahedral		
5	trigonal bipyramid		
6	octahedral		

Figure 1.11
SHAPES OF MOLECULES FROM VSEPR THEORY.

ORGANIC Chemistry Now™
Click *Molecular Models* to view the molecules in this book as interactive three-dimensional models.

Figure 1.12

THE SHAPE OF METHANE, CH_4.

Ball-and-stick model of methane
(Atoms are not shown to size.)

Space-filling model of methane
(Correct relative sizes of atoms are shown.)

Important Convention

front of the page; others extend behind the page. *Commonly, a heavy wedged line is used to represent a bond that extends in front of the plane of the page and a dashed wedge line is used to represent a bond that extends behind the plane of the page.* These conventions are used to show the shapes of the molecules in Figure 1.11. Figure 1.12 shows some other pictures for the tetrahedral molecule CH_4. It is common for students to have difficulty picturing the actual three-dimensional shapes of the molecules from these two-dimensional drawings. It is a good idea to work with a set of models until the process becomes easier. The computer-generated molecular models on the web page (http://now.brookscole.com/hornback2) are also very useful for picturing shapes.

▶ RULE 2

An unshared pair of electrons repels other pairs more than a shared pair of electrons does. This seems reasonable because a shared pair, which also spends time around another atom, should not offer as much charge concentration for repulsion as a pair of electrons that is not shared and therefore spends all of its time around the atom.

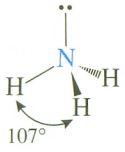
Consider the shape of ammonia, NH_3, shown in Figure 1.13. Ammonia has four pairs of electrons in its valence shell: three shared pairs and one unshared pair. These four pairs of electrons have a basic tetrahedral arrangement. However, because the unshared pair repels more than the shared pairs do, the shared pairs are pushed closer together, and the bond angles are 107° rather than the exact tetrahedral bond angle of 109.5°. Usually, the location of the atoms in a molecule, not the position of electrons, is shown, so ammonia is termed a *pyramidal molecule;* that is, the nitrogen and the three hydrogens form a pyramid. Figure 1.13 also shows the shape of water. Again there are four pairs of electrons that have a basic tetrahedral arrangement. The two unshared pairs push the shared pairs even closer together. The result is that water is a bent molecule with a bond angle of 105°.

▶ RULE 3

Double and triple bonds are treated as one shared pair of electrons.

Several examples of the use of this rule are shown in Figure 1.14.

By using additional rules from VSEPR theory, we can make more exact predictions about the shapes of molecules. For example, the HCO bond angle of CH_2O can be pre-



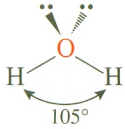
Ball-and-stick model

Space-filling model

Figure 1.13

THE SHAPES OF (a) AMMONIA AND (b) WATER MOLECULES.

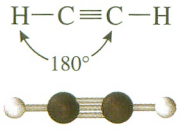
(a) The three shared pairs of electrons and the unshared pair of ammonia are arranged in a tetrahedral manner around the nitrogen. The resulting geometry of the nitrogen and the three hydrogens is a pyramid. The HNH bond angle is less than 109.5° (the tetrahedral bond angle) because the unshared electron pair behaves as though it is larger than the electron pairs in the bonds.



Ball-and-stick model

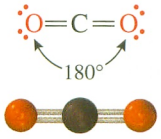
Space-filling model

(b) The two shared pairs of electrons and the two unshared pairs of water are also arranged in a tetrahedron. The resulting geometry of the three atoms is bent, with the HOH angle even smaller (105°) because of the repulsion of two unshared electron pairs.



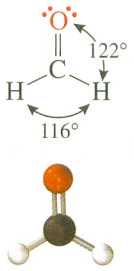
Ethyne

(a) The triple bond counts as one pair of electrons for the purposes of VSEPR theory. Therefore, each carbon has two pairs. The geometry is linear around each carbon and linear overall.



Carbon dioxide

(b) Each double bond counts as one pair of electrons. Therefore, the carbon has two pairs, and the geometry is linear.



Formaldehyde

(c) The double bond counts as one pair, so the geometry about the carbon is trigonal planar. The predicted bond angles are 120° Actually, the HCO angle is 122°. Such minor deviations should be expected because the bonds are not the same and therefore are not necessarily the same "size." In fact, a double bond to an oxygen might be expected to be "larger" than a single bond to a hydrogen.

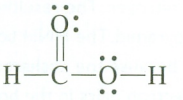
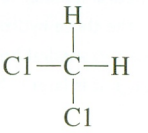
Figure 1.14

THE SHAPES OF (a) ETHYNE, C_2H_2; (b) CARBON DIOXIDE, CO_2; AND (c) FORMALEDHYDE, CH_2O.

dicted to be slightly greater than 120°, as shown in Figure 1.14. However, we will not need to know geometries that accurately. It is enough to know that the geometry of CH_2O is approximately trigonal planar.

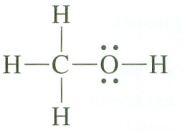
PROBLEM 1.12

Predict the geometry at the carbon of these compounds:

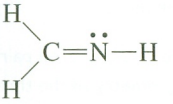
a) H—C≡N: **b)**  **c)** 

PROBLEM 1.13

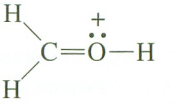
Predict the geometry of the following compounds at the indicated atoms:

a) 

At the carbon
At the oxygen

b) 

At the carbon
At the nitrogen

c) 

At the carbon
At the oxygen

MODEL-BUILDING PROBLEM 1.1

Build models of these compounds with a handheld model kit and note their geometries:

a) CH_4 **b)** BF_3 **c)** NH_3 **d)** H_2O **e)** PCl_5
f) C_2H_2 **g)** CH_2O

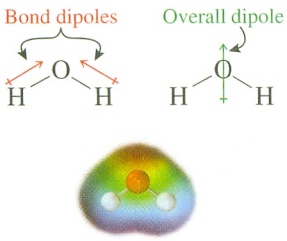
MODEL-BUILDING PROBLEM 1.2

Build models of the compounds shown in problem 1.13 and note their geometries.

1.11 Dipole Moments

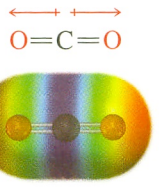
The overall dipole moment of a molecule is the vector sum of the individual bond dipoles. If the shape of a molecule is known, vector addition can be used to predict the direction of the dipole moment of that molecule. Several examples are shown in Figure 1.15. The predictions agree with experimental results. For example, CO_2 is found by experiment to have a dipole moment of zero. It is a nonpolar molecule. Because the bonds are polar, this is possible only if the bond dipoles cancel. Therefore, CO_2 must be a linear molecule. On the other hand, because water is polar, with a dipole moment of 1.8 D, it cannot be a linear molecule. A molecule that has only relatively nonpolar carbon–carbon and carbon–hydrogen bonds has only a small dipole moment, if any, and is said to be nonpolar.

These computer-generated electrostatic potential maps use color to show the calculated electron density in a molecule. Electron-rich regions are red and electron-poor regions are blue.



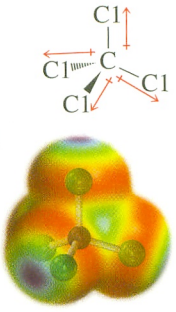
Electrostatic potential map for water (H_2O)

The individual bond dipoles of water are shown in the left structure. The vector sum shown in the right structure indicates the direction of the overall dipole moment of the molecule. Its magnitude is 1.8 D.



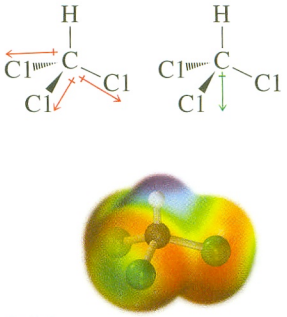
Electrostatic potential map for carbon dioxide (CO_2)

The individual bond dipoles of CO_2 point in opposite directions. These cancel on vector addition, so this compound has a dipole moment of zero.



Electrostatic potential map for carbon tetrachloride (CCl_4)

Although it is more difficult to see, the individual bond dipoles of CCl_4 also cancel on vector addition, and the overall dipole moment is zero.



Electrostatic potential map for trichloromethane ($HCCl_3$)

For $HCCl_3$ the individual bond dipoles, shown in the first structure, add to give an overall dipole moment of 1.9 D with the direction shown in the second structure.

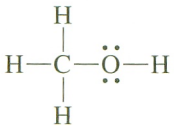
Active Figure 1.15

ORGANIC Chemistry Now™

OBTAINING DIPOLE MOMENTS FROM BOND DIPOLES. Test yourself on the concepts in this figure at **OrganicChemistryNow.**

PRACTICE PROBLEM 1.4

Predict the direction of the dipole moment in this compound:

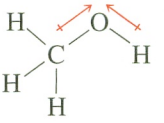


Strategy

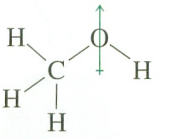
Use VSEPR theory to determine the geometry at each atom and the overall shape of the molecule. Then determine which bonds are polar based on the electronegativity differences of the atoms. Put in the directions for individual bond dipoles of these bonds. Estimate the result of vector addition of the bond dipoles to get the approximate direction for the overall dipole for the molecule.

Solution

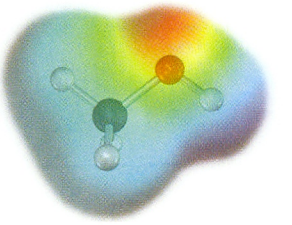
In problem 1.13 we found that the geometry at the carbon of this molecule, with four bonding pairs of electrons, is tetrahedral. The geometry of the electron pairs at the oxygen (two unshared pairs and two shared pairs) is also tetrahedral, so the geometry of the C—O—H atoms is bent. The C—H bonds are nonpolar, but the O—H and O—C bonds are both polar with the negative end of the bond dipole at the oxygen because oxygen is more electronegative than either carbon or hydrogen. Vector addition gives the overall dipole moment shown here.



Bond dipoles

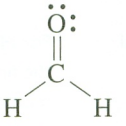


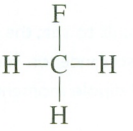
Overall dipole

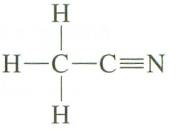


PROBLEM 1.14

Predict the direction of the dipole moments of these compounds:

a) 

b) 

c) 

In the next chapter the simple bonding picture that has been developed here will be used to help understand and predict which molecules are stable. We will also begin to learn how the structure of a molecule affects its physical and chemical properties.

ORGANIC Chemistry Now™
Click *Mastery Goal Quiz* to test how well you have met these goals.

Review of Mastery Goals

After completing this chapter, you should be able to:

- Write the best Lewis structure for any molecule or ion. This includes determining how many electrons are available and whether multiple bonds are necessary and satisfying the octet rule if possible. For complex molecules, however, the connectivity must be known. (Problems 1.15, 1.16, 1.17, 1.24, 1.29, 1.30, and 1.31)

- Calculate the formal charge on any atom in a Lewis structure. (In fact, you should be starting to recognize the formal charges on some atoms in some situations without doing a calculation.) (Problems 1.18, 1.26, and 1.30)
- Estimate the stability of a Lewis structure by whether it satisfies the octet rule and by the number and the distribution of the formal charges in the structure. (Problems 1.19, 1.20, and 1.36)
- Recognize some simple cases in which resonance is necessary to describe the actual structure of a molecule. However, a better understanding of resonance will have to wait until Chapter 3. (Problems 1.23, 1.25, 1.34, 1.35, and 1.39)
- Arrange the atoms that are of most interest to organic chemistry in order of their electronegativities and assign the direction of the dipole of any bond involving these atoms. (Problems 1.21 and 1.37)
- Determine the shape of a molecule from its Lewis structure by using VSEPR theory. (Problems 1.21, 1.22, 1.24, 1.29, 1.34, 1.35, and 1.36)
- Determine whether a compound is polar or not and assign the direction of its dipole moment. (Problems 1.21, 1.24, and 1.38)

Additional Problems

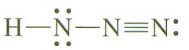
ORGANIC Chemistry Now™
Assess your understanding of this chapter's topics with additional quizzing and conceptual-based problems at **http://now.brookscole.com/hornback2**

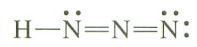
1.15 Explain whether the bonds in these compounds would be ionic or covalent and show Lewis structures for them:
a) KCl **b)** NCl_3 **c)** NaCN **d)** KOH

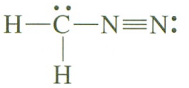
1.16 What is the formula for the simplest neutral compound formed from P and H? Show a Lewis structure for this compound and predict its shape.

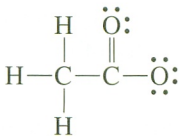
1.17 Show Lewis structures for these compounds:
a) CH_5N **b)** C_2H_5Cl **c)** N_2 **d)** CH_2S
e) C_2H_3F **f)** CH_4S

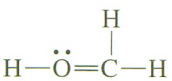
1.18 Calculate the formal charges on all of the atoms, except hydrogens, in these compounds:

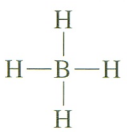
a) 

b) 

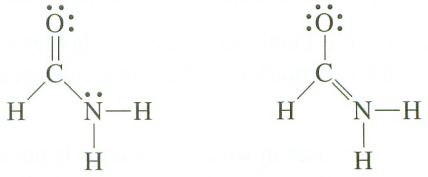
c) 

d) 

e) 

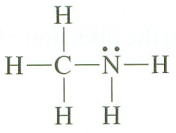
f) 

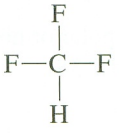
1.19 Explain which of the two following structures would be more stable. Explain whether they represent isomers or are resonance structures.

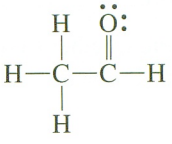


1.20 Draw a Lewis structure for carbon monoxide (CO). Calculate the formal charges on the atoms and comment on the stability of this compound.

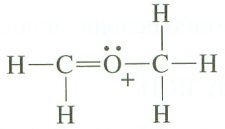
1.21 Use heavy and dashed wedged lines to show the shapes of the following molecules. Show the bond dipole of each polar bond and show the overall dipole of each molecule.

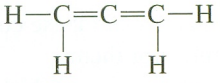
a) 

b) 

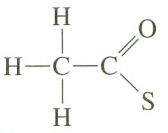
c) 

1.22 Predict the geometry at each atom, except hydrogens, in these compounds:

a) 

b) 

1.23 **a)** Show the unshared electron pairs on the following anion. The S has a formal charge of −1, and the formal charges of the other atoms are zero.

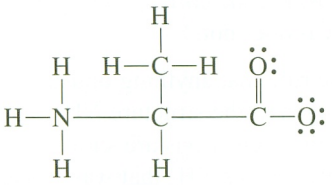


b) Draw a resonance structure for this ion.

1.24 Show a Lewis structure for C_2H_6O in which both carbons are bonded to the oxygen. What is the geometry of this molecule at the oxygen? Show the direction of the dipole for the molecule.

1.25 Show a Lewis structure for NO_2^-. (Both oxygens are bonded to the nitrogen.) Show a resonance structure also.

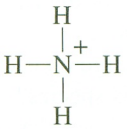
1.26 Amino acids, from which proteins are formed, exist as "dipolar ions." The structure of the dipolar ion of the amino acid alanine is



Alanine

a) Calculate the formal charges on all of the atoms, except hydrogens, of alanine.
b) What is the overall charge of alanine?
c) Explain whether or not you expect the two oxygens to be different.

1.27 A covalent ion can also have polar bonds. Consider the ammonium cation. How are its bonds polarized? Do you think that the N of the ammonium cation is more or less "electronegative" than the N of ammonia (NH_3)? Would the hydrogens of NH_4^+ or NH_3 have a larger partial positive charge?



Ammonium cation

1.28 You need to know the melting point for $CaCl_2$ for a lab report you are writing. Your lab partner says that the *Handbook of Chemistry and Physics* lists this as 68°C. Do you think you should trust that your lab partner has looked up the value correctly or should you look it up for yourself?

1.29 Show a Lewis structure for $AlCl_4^-$. What are the formal charges on the atoms of this anion? What is its shape?

1.30 Ammonium cyanate is composed of an ammonium cation (NH_4^+) and a cyanate anion (OCN^-). Show a Lewis structure for the cyanate anion. (Both O and N are bonded to C.) Which atom has the negative formal charge in your structure? What is the shape of the ion? Show a resonance structure for this ion.

1.31 **a)** Show a Lewis structure for urea, CH_4N_2O. Both N's and the O are bonded to the C. The H's are bonded to the N's. None of the atoms has a formal charge.
b) Show a Lewis structure of an isomer of urea that still has both N's and the O bonded to the C and has formal charges of zero at all atoms.

1.32 Phosphorus forms two compounds with chlorine, PCl_3 and PCl_5. The former follows the octet rule, but the latter does not. Show Lewis structures for each of these compounds. For the corresponding nitrogen compounds, explain why NCl_3 exists but NCl_5 does not.

1.33 On the basis of the rule that anything unusual about a structure must be shown explicitly, the nitrogen in the structure NH_3 is seen to have an unshared pair of electrons whether these electrons are shown or not. Suppose you wanted to discuss the unstable species NH_3 that was missing the unshared pair of electrons. How would you draw the structure so that it would be obvious to another person that the unshared pair was absent?

1.34 Ozone, O_3, is a form of oxygen found in the upper atmosphere. It has the connectivity O—O—O and is neutral.

a) Show a Lewis structure for ozone.
b) Calculate the formal charge on each oxygen of ozone.
c) What is the shape of ozone?
d) Experimental observations show that both bonds of ozone are identical. Explain how this is possible.

1.35 **a)** Draw a Lewis structure for the carbonate anion CO_3^{2-}. Each oxygen is bonded only to the carbon.
b) Calculate the formal charge on each atom.
c) What is the shape of this species?
d) Experimental evidence shows that all of the oxygens are identical. Explain.

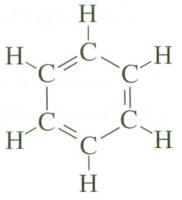
1.36 Consider the species CH_3, which has three normal carbon–hydrogen bonds and no other electrons on the carbon.

a) What is the charge of this species?
b) What is its geometry?
c) Discuss the stability of this species. Do you think it is more or less stable than the species shown in practice problem 1.1? Explain.
d) Show the Lewis structure of the product of the reaction of this species with hydroxide ion (OH^-).

1.37 Explain how the dipole moments of FCl (0.9 D) and ICl (0.7 D) can be so similar.

1.38 Chlorine is more electronegative than phosphorus. Predict the dipole moment of PCl_5.

1.39 Although carbon–carbon double bonds are shorter than carbon–carbon single bonds, all of the carbon–carbon bonds of benzene are the same length. Explain.



Benzene

1.40 Explain whether or not these molecules are polar (have a dipole moment).

a) CBr_4 **b)** NH_3 **c)** CH_3OCH_3

d) CH_2Cl_2 **e)** CO_2

Problems Using Online Three-Dimensional Molecular Models

ORGANIC Chemistry Now™
Click *Molecular Model Problems* to view the models needed to work these problems.

1.41 For each model, draw a structure that fits the geometry of the molecule. Then explain the geometry at each atom other than the hydrogens.

1.42 Draw a structure for each model. Explain whether the molecule represented by each model has a dipole moment or not.

1.43 Draw a structure for each model. Show the direction of the dipole moment for the molecule represented by each model.

1.44 Draw a structure for the model. Is the molecule polar or nonpolar? Explain.

vMentor™ Do you need a live tutor for homework problems? Access vMentor at Organic ChemistryNow at **http://now.brookscole.com/hornback2** for one-on-one tutoring from a chemistry expert.